

# SPECIFICATION

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## Prevention of Contamination on Plated Wafer Surfaces

### Background of the Invention

[0001] FIELD OF THE INVENTION

[0002] The present invention generally relates to electroplating or electrolysis plating of metals or metal-containing alloys on wafer substrates and more specifically to a method for preventing salt precipitation after such a plating process and a corresponding plating solution.

[0003] BACKGROUND OF THE INVENTION

[0004] During production of a plating layer on a wafer or the like, the wafer after the plating process occasionally becomes contaminated by plating constituents. Contaminants frequently found are hydroxides or sulfates, respectively, of the plated metals. Some of these salts can cause long term corrosion leading to failures of the later product.

[0005] Thus, a dissolution in an additional post-cleaning step becomes necessary. Post-treatment cleaning after electroplating is conventionally performed by applying either organic solvents or a high amount of ultra-clean (de-ionized) water on the wafer surface combined with a variety of physico-mechanical treatment processes (see e.g. W. Kern, "Handbook of Semiconductor Wafer Cleaning Technology", Noyes Publications, Westwood, NJ, USA, 1993). However, this method requires the following:

[0006] – high amounts of ultra-pure water (or organic solvents);

[0007] – a guaranteed high flow of the cleaning solution;

[0008] – a large distance between the plating and rinsing area to avoid cross-

contamination.

[0009] In some cases, this cleaning is not effective. Salt particles precipitate at the wafer surface, which acts as a crystallization point. It was found that these particles might be corrosive and destroy the later product. For this reason, an additional cleaning step is necessary to remove the particles.

[0010] A first approach commonly known as the "RCA" cleaning process deals with the dissolution of metal and/or metal salts settled down to the surface of silicon wafers in the semiconductor industry. In the RCA cleaning process, the wafer surface is treated oxidatively with an alkaline complex former solution wherein, most frequently, hydrogen peroxide ( $H_2O_2$ ) is the oxidant. It was shown that magnesium salts or zinc metal particles can successfully be removed from a silicon surface by way of the RCA process.

[0011] According to a second known approach proposed by I. Hayashida et al. in U.S. Patent No. 5,290,361 entitled "Surface Treating Cleaning Method", dissolution and complexation are performed in the same step.

[0012] In a third known approach disclosed in U.S. Patent No. 5,637,151 by P. Schulz entitled "Method for Reducing Metal Contamination of Silicon Wafers During Semiconductor Manufacturing", the above mentioned two processes are separated into two individual steps. The process according to Schulz can only be successfully performed if the wafer surface is chemically inert when exposed to the cleaning solution.

[0013] This kind of treatment cannot be applied if the contaminants and wafer surface are chemically similar. This is always the case for plating processes, where, for example, nickel salts settle down on a nickel-containing surface. In this case, the cleaning solution also attacks the wafer surface.

[0014] Further, known approaches which deal with acidic cleaning processes during electroplating are directed to the pre-cleaning steps before plating. For example, U.S. Patent No. 5,843,538 by R. Ehram et al. entitled "Method for Electroless Nickel Plating of Metal Substrates" describes a pre-cleaning of a machined metal substrate with the help of an organic acidic solution. The aim is to remove especially solid

organic contaminants to guarantee reasonable plating. In addition, U.S. Patent No. 5,373,629 by J. Hupe et al. entitled "Through-hole Plate Printed Circuit Board with Resist and Process for Manufacturing Same" proposes to remove solid metal contamination resulting from a mechanical process with an acidic solution before plating. Thereupon, in an article by O. J. Anttila and M. V. Tilli published in J. Electrochem. Soc. 139, 1992, 1751, entitled "Metal Contamination Removal on Silicon Wafers Using Dilute Acidic Solutions" describes a pre-cleaning with oxidizing, slightly acidic solutions to remove metal contamination. The aim of this described technique is to oxidize the metallic material and to dissolve the formed oxides "in-situ". Further, a multi-step plating process in which an activation (= chemical modification) of the surface is performed between the different steps is described in U.S. Patent No. 5,849,170 by S. Djokic et al. entitled "Electroless/Electrolytic Methods for the Preparation of Metallized Ceramic Substrates". The activation is performed by either an acidic palladium chloride or an acidic tin chloride solution. But the activation thereby leads to a chemical modification (chemical attack) of the surface.

[0015] The above cited cleaning processes at acidic pH values under oxidizing conditions might lead to a chemical modification of the electroplated film. In some cases, this modification is desired (e.g. U.S. Patent No. 5,849,170), but in most cases, the contact of metallic films with oxidizing acids lead to the disadvantageous process of corrosion. It is further known that nearly all acids attack nickel alloys in a more or less high degree under these conditions. For example, oxidizing chloride solutions lead to dangerous pitting corrosion, a localized form of corrosion starting after short times and leading to deep holes in the surface. Other acids (e.g. nitric acid) lead to an intergranular attack followed by homogenous corrosion.

[0016] In the case of wafer technology, the thickness of the plated films normally is in the range of a few micrometers. Thus, such films are extremely susceptible to surface modification reactions, which are caused by corrosion processes. The electroplated films on wafers:

[0017] – have to be strictly planar (i.e. they may not comprise pits);

[0018] – must be of a defined thickness (i.e. post-plated dissolution must be avoided);

[0019] - must have a surface film of known structure and composition (i.e. oxides).

[0020] Thus, in conventional electroplating processes, the post-cleaning of the plated wafers is performed by introduction of de-ionized water onto the wafer surface to remove the remaining plating solution. In disadvantageous conditions, for example, if the water flow is too low, a precipitation of inorganic salts occurs and the wafer becomes contaminated with particles. In other words, the only way to remove any contamination contained in the plating solution is to clean the wafer surface with a large amount of de-ionized water.

## Brief Summary of the Invention

[0021] It is therefore an object of the present invention to provide a method for preventing salt precipitation after plating which is highly effective and simple, and thus cost effective to implement.

[0022] The proposed method prevents the formation of contamination at an early stage after the plating process and thus advantageously avoids solid contamination on the wafer surface without requiring an additional dissolution step to clean the surface. Any metal contamination after plating which can precipitate on the wafer surface is retained in the plating solution by introducing a stabilizer which either is a complex former, or an acid, or a combination of a complex former and an acid. It is emphasized hereby that the metal contamination, according to the invention, is retained in the plating solution but not in the cleaning solution as in the recited prior art approaches. The stabilizer hereby is applied on the wet wafer surface after the plating process. Thus, no additional step to dissolve precipitated salts from the surface is necessary.

[0023] In a first embodiment, the solubility of metal ions is drastically increased by application of a complex former to inhibit precipitation of salts. The complex former can be of an organic (e.g. citrate, ethylenediaminetetraacetate (EDTA)), or inorganic (e.g.  $\text{NH}_3$ ) nature.

[0024] In a second embodiment, application of an acidic solution additionally avoids a "pH shock", which occurs when water is used as a cleaning substance to remove the acidic plating solution. A sudden increase of pH value would lead to a precipitation of

hydroxides or sulfates of the plated metals.

[0025] In contrast to the prior art approaches, the present invention prevents the occurrence of solid contamination on the wafer surface. Thus, an additional dissolution or complexing step becomes unnecessary and thus the proposed procedure is not aggressive against the freshly plated surface, in contrast to the additional dissolution or complexing steps according to the prior art which have to dissolve particular materials from the surface and for that reason automatically attack the chemical similar surface.

[0026] Thereupon, powerful complex formers already present in the plating solution can also prevent the metal salts from precipitation in the later rinse process. Such complex formers are, for example, EDTA, which have a high complexing capacity for the plated metals. Thus, the metals are also kept in solution during a post-plating rinse with water, when the concentration of the complex former is drastically reduced.

## Brief Description of the Several Views of the Drawings

[0027] The present invention is described in more detail with reference to the following figures.

[0028] Figs. 1A-B show two possible scenarios for the formation of precipitated contamination during a plating process performed on a wafer surface;

[0029] Fig. 2 shows a comparison of a conventional process for wafer cleaning with a first embodiment of the cleaning process according to the present invention wherein the conventional cleaning of a contaminated wafer by dissolution and complexation of the solid particles is covered by U.S. Patent No. 5,637,151;

[0030] Figs. 3A-D depict a second embodiment of a cleaning process of the present invention applied to a wafer surface already covered with a plating solution; and

[0031] Figs. 4A-D depict a third embodiment of a cleaning process of the present invention applied to a wafer surface also covered with a plating solution.

## Detailed Description of the Invention

[0032] DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0033] Referring to Fig. 1, the origin of contamination of a wafer surface 4 with precipitating salts is described by the results of micro-analysis experiments performed in a nickel-iron plating process. In such a plating process mostly basic nickel sulfates, or nickel and iron hydroxides, respectively, are precipitated. In particular, the sulfates are known for their corrosion-inducing character and therefore need to be eliminated.

[0034] The conventional cleaning used in plating processes performed exclusively with de-ionized water in a space-restricted plating tool comprised up to 3% of the active area of the wafer 2 was contaminated with salt precipitates. Long term corrosion tests have proven the corrosive character of these precipitates. The origin of these particles can be chemically explained by a precipitation of low-soluble salts of both nickel and iron (sulfates, hydroxides). This happens, when either of the following occurs:

[0035] – the remaining plating solution 6 suddenly comes in contact with a high amount of de-ionized water 8 (see Fig. 1A); or,

[0036] – a wet wafer (a wafer 2 with de-ionized water 10 on the wafer surface 4) stays in contact with a dirty atmosphere where droplets / aerosols of plating solution 12 are present (see Fig. 1B).

[0037] If the agitation velocity of the cleaning water 8 is not sufficiently high during the whole cleaning process, the precipitates are able to settle down and age at the wafer surface 4. After a brief amount of time, only a few minutes, it is not possible to remove the precipitates even with powerful cleaning procedures (e.g. spin-rinse cleaner with hot water). To avoid corrosion problems in later applications, the affected active areas of the wafer 2 have to be selected carefully and removed prior to subsequent processes which requires an enormous amount of time.

[0038] According to the present invention, salt precipitation is prevented by a chemical modification of the cleaning strategy as follows:

[0039] – by applying a solution of a complex former; or,

[0040] – by applying an acidic solution; or,

[0041] – by applying an acidic aqueous solution of a complex former.

[0042] The results of these experiments are summarized in Table 1 which depicts the amount of contamination obtained after different cleaning strategies.

[t1]

**Table 1:** Amount of contamination measured after different cleaning strategies.

<u>Cleaning Procedure</u>	<u>Contaminated Area (%)</u>
Pure Water	Up to 3
Citrate	0
Acetate	0
EDTA	0
Ammonia	0
Hydrochloric Acid	0
Phosphoric Acid	0
Sulfuric Acid	Up to 10
Sulfuric Acid / EDTA	0

[0043] A comparison between a conventional process for wafer cleaning known in the prior art and a first embodiment of the process according to the present invention is accomplished with reference to Fig. 2. The conventional cleaning 14 of a contaminated wafer 20 by dissolution 21 and complexation 22 of the solid particles is covered by U.S. Patent No. 5,637,151.

[0044] The present invention 16 introduces the complexation step 22 directly after the plating step 18. This avoids the need for the dissolution step 21, which is necessary, if salt precipitation has occurred. Additionally, it prevents detrimental surface attack caused by the dissolution step 21.

[0045] Fig. 3 depicts a second embodiment of a cleaning process of the present invention applied to a wafer 2 covered with plating solution 6 where a complex former solution 26 is applied to the wafer surface 4. The presence of a suitable complex former solution 26 enhances the solubility of heavy metal salts typically by orders of magnitudes. Consequently, a precipitation of these salts is not observed in such solutions. After plating, the wafer 2 is covered with a plating solution 6 as shown in Fig. 3A. In a first cleaning step, the complex former solution 26 is applied on the wafer surface 4. This procedure reduces the amounts of plating salts in the solution

and keeps the solubility of the remaining salts high at the same time due to a formation of soluble metal complexes. Next, the wafer 2 is completely covered with a clean complex solution 26 as shown in Fig. 3B. Fig. 3C shows the complex solution 26 is removed in a following step by a stream of de-ionized water (not shown), leading to clean water 28 covering wafer 2. The drying of the wafer can be performed in a conventional procedure (e.g. spin dryer) resulting in a clean, dry wafer 30 as shown in Fig. 3D.

[0046] In our experiments, the following aqueous solutions of different complex formers 26 were applied in various concentrations:

[0047] - Citrate (concentration 0.5–1.0 mol/kg);

[0048] - Acetate (concentration 0.5 mol/kg);

[0049] - EDTA (concentration 0.2–0.5 mol/kg);

[0050] - Ammonia (concentration 0.1–1.0 mol/kg).

[0051] - Hydrochloric acid

[0052] - Phosphoric Acid

[0053] In the case of all of the complex formers 26 listed above, no occurrence of particles was observed after the total cleaning procedure.

[0054] In the following, a third embodiment of applying an acidic solution 32 to the wafer surface 4 is described by referring to Fig. 4. The solubility of most salts is strongly influenced by the pH value of the solution. For example, freshly precipitated heavy metal hydroxides can easily be dissolved in an acidic solution, but they are nearly insoluble in neutral or alkaline solutions. Also the dissolution rate of aged precipitates is strongly reduced. Consequently, the procedure described in the second embodiment can also be applied by an introduction of an aqueous solution of a suitable acid 32. This third embodiment is illustrated in Fig. 4.

[0055] In our experiments, the following aqueous solutions of different acids 32 were applied:



[0056] – Hydrochloric Acid (concentration 0.1 mol/kg);

[0057] – Hydrochloric Acid (concentration 0.01 mol/kg);

[0058] – Sulfuric Acid (concentration 0.05 mol/kg);

[0059] – Phosphoric Acid (concentration 0.1 mol/kg).

[0060] In the case of hydrochloric and phosphoric acids, respectively, no particles were observed after the total cleaning procedure. The application of sulfuric acid led to an occurrence of nickel sulfate precipitation and thus contamination of the wafer 2 (up to 10% of the surface). Thus, sulfuric acid does not lead to successful cleaning.

[0061] According to a fourth embodiment, an acidic complex former solution 32 is applied to a wafer surface. An experiment was performed with a mixture of aqueous sulfuric acid (0.05 mol/kg) and EDTA solution (0.5 mol/kg). No precipitation was observed on the wafer 2. This means that the complexing power of the EDTA is high enough to prohibit a precipitation of nickel sulfate.

[0062] It is noted that the plating process according to the invention, besides wafer substrates, can also be applied to other types of substrates where a plating by the mentioned chemical components can be fulfilled. In accordance, the proposed plating process includes electroplating or electrolysis plating or similar mechanisms.

[0063] Further, it is emphasized that the above described complex former(s) advantageously can be already contained in the plating solution thus simplifying the plating process and further enhancing the efficiency of the proposed method since precipitation of inorganic contamination is suppressed from the start of the plating process and throughout.